



Modeling Superconformal Electrodeposition Using The Level Set Method

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Superconformal deposition enables the void-free filling of high aspect ratio features such as trenches or vias in the Damascene metallization process. Superconformal electrodeposition, also known as superfill, occurs when particular combinations of chemical additives are included in the electrolyte. The additives enable preferential metal deposition at the bottom surface which leads to bottom up filling before the sidewalls close off. Two crucial mechanisms by which the additives enable superfill to occur are (i) accelerator behavior increasing the copper deposition rate as a function of coverage and (ii) conservation of accelerator coverage with increasing/decreasing interface area. Thus, the adsorbed catalytic accelerator species floats upon the growing metal/electrolyte interface. An effective modeling approach must accurately track the position of the interface as well as preserving surfactant coverage while the interface is advancing. This must be achieved in an Eulerian framework due to the necessity of modeling the diffusion of electrolyte species. To this end, the level set method is used to track the interface while a scalar variable approach governs the surfactant coverage. Modeling of additive accumulation and conservation on a deforming interface in conjunction with the level set method presents areas for novel numerical approaches. Several test cases are examined to validate the surface coverage model. Comparison of superfilling simulations with experimental results is also presented.

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Damascene copper is rapidly replacing aluminum as the interconnect material of choice in silicon technology. The change is driven by the lower electrical resistivity of copper, which exhibits improved resistance to electromigration, decreasing power consumption, and increasing central processor unit (CPU) clocking speeds. Electroplating is the preferred deposition method because it permits filling of high-aspect ratio features without seams or voids through the process of superconformal deposition, also called superfill. This process has been demonstrated to depend critically on the inclusion of additives in the electrolyte.¹ Recent publications propose curvature enhanced accelerator coverage (CEAC) as the mechanism behind the superfilling process.² In this mechanism, molecules that accelerate local metal deposition displace molecules that inhibit local metal deposition on the metal/electrolyte interface. For electrolytes that yield superconformal filling of fine features, this buildup happens relatively slowly because the concentration of accelerator species is much more dilute compared to the inhibitor species in the electrolyte. The mechanism that leads to the increased rate of metal deposition along the bottom of the filling trench is the concurrent local increase of the accelerator coverage due to decreasing local surface area, which scales with the local curvature (hence the name of the mechanism).

Previous modeling of copper deposition utilized leveling theory that only considered spatially varying accumulation of inhibiting additives induced by concentration gradients within the electrolyte.^{3,4} One group utilized a leveling model with the boundary element method to predict the filling of triangular and semicircular grooves.⁵ Those results demonstrated the importance of specimen geometry alone on filling, the so-called geometric leveling effect. However, such leveling theories could not self-consistently explain superconformal filling of submicrometer, high-aspect ratio features. With all leveling models, rapid deposition also occurs on the sides approaching the bottoms of the features, rather than only on the bottom as is generally acknowledged to be the case in experimental studies. Furthermore, leveling models do not predict an incubation period of conformal growth prior to superfill or development of a bump over the features after superfill, both well known experimentally.

The CEAC mechanism, implemented using a string model (particle marker method) to track the interface, was recently shown to predict superconformal deposition for aspect ratios up to five (for

the conditions studied).² More importantly, this work predicted the previously unexplained incubation period and overfill bump. The predictions of the CEAC-based model agreed well with experimental results across a large range of electrolyte compositions, deposition voltages, and trench aspect ratios with no fitting parameters. The string model neglected diffusion-induced concentration gradients within the electrolyte. A string implementation of a different mechanism for additive accumulation was subsequently published; kinetic parameters were optimized by fitting the results of a particular fill experiment.⁶ Most recently preliminary results of the study described in this paper were published.⁷ That work presented a more complete description of the kinetics of additive accumulation than those first used with the CEAC mechanism.² Filling results agreed well with experimental results across a large range of electrolyte compositions, deposition voltages, and trench aspect ratios. As with the earlier application of the CEAC mechanism, this feature filling was modeled with no fitting parameters.³

Modeling of copper deposition with implementation of the CEAC model requires simultaneous tracking of the copper/electrolyte interface location and shape, surface coverage of the adsorbed additives, and the spatially varying concentration profiles of the different components in the electrolyte. The evolution of the adsorbed accelerator coverage is determined from these quantities by a conservation equation which accounts for the change of surface area, influx from the electrolyte, and consumption into the metal. The local interface velocity is determined from the accelerator coverage via a rate equation. Concentrations within the electrolyte satisfy diffusion equations.

This paper presents a computational solution to this modeling problem. The level set method (LSM) is used to track the copper/electrolyte interface on a mixed grid. Determination of the time-dependent accelerator coverage adsorbed on the interface is accomplished by evolution of a scalar concentration variable defined throughout the domain.

In the LSM a scalar variable, ϕ , is defined over the entire region. The set of locations $\phi = 0$, (i.e., the zero level set), defines the position of the interface. The variable ϕ is continuous, smooth, and monotonic in the direction normal to the interface and is maintained as a distance function⁸ throughout the calculation, allowing the distance between any point in the solution domain and the interface to be known. The interface thus remains at a steady thickness, deter-

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^a The early code,⁷ though containing an error that led to unphysical behavior at the top corners of the filling features, still gave accurate prediction of whether the particular features studied filled or failed to fill.

mined by local grid spacing, eliminating smearing of the interface. The distance function is initialized once at the start of the simulation using the fast marching method. Thereafter the use of extension velocities and the correct discretization of the advection equation maintains the distance function. The LSM has already been shown to be a useful method for a variety of deposition processes in a trio of articles by Adalsteinsson and Sethian.⁹⁻¹¹

The authors believe that the combination of the LSM and CEAC mechanisms presented here represents a novel method that may be applicable to a number of other adsorption problems. Several validation tests that demonstrate the accuracy of the solution for problematic high-curvature interfaces are presented as is comparison of prediction with experimental fill results.

Model Specification

The local interface velocity is expressed in terms of the local deposition current density i by⁷

$$\mathbf{v} = \frac{i\Omega\mathbf{n}}{2F} \quad [1]$$

where $\mathbf{n}$, Ω , and F are the normal to the interface pointing into the electrolyte, the atomic volume of the depositing metal, and Faraday's constant respectively. The 2 is the formal charge of cupric ion (Cu^{2+}). For practical plating conditions, the current density i is given by the Butler-Volmer equation⁷

$$i = i_0 \frac{c_c^i}{c_c^\infty} \exp\left(-\frac{\alpha F}{RT} \eta\right) \quad [2]$$

where i_0 , c_c^i , c_c^∞ , α , R , T , and η are the exchange current density, the molar concentration of copper at the interface, the molar concentration of copper in the far field, the transfer coefficient (a measure of the symmetry of the energy barrier), the gas constant, the temperature, and the overpotential, respectively. Dependence of Eq. 2 on the accelerator coverage adsorbed at the metal/electrolyte interface, θ , is determined experimentally from (i - η) studies of deposition on flat copper electrodes independent from trench filling experiments. The dependencies are given by^{2,7}

$$i_0(\theta) = b_0 + b_1\theta \quad [3]$$

and

$$\alpha(\theta) = m_0 + m_1\theta \quad [4]$$

The rate of change of accelerator coverage, θ , depends on interface area evolution, adsorption from the electrolyte, and deactivation by slow consumption into the metal. The conservation of accelerator species is given by

$$\frac{d}{dt} \int_u \theta dA_u = \int_u (J_a - J_d) dA_u \quad [5]$$

where A_u represents the interface area and J_a and J_d are the fluxes due to adsorption and consumption, respectively. The consumption flux represents the accelerator absorbed into the metal as distinct from that which remains on the surface. The subscript u indicates an integral moving with the interface. The adsorption flux is given by

$$J_a = \frac{k_a}{\Gamma_0} (1 - \theta) c_m^i \quad [6]$$

where k_a , c_m^i , Γ_0 are the jump frequency or rate constant, the accelerator concentration in the electrolyte at the interface, and the surface site density on the interface, respectively. Equation 6 takes the form of Langmuir adsorption with $(1 - \theta)$ representing the

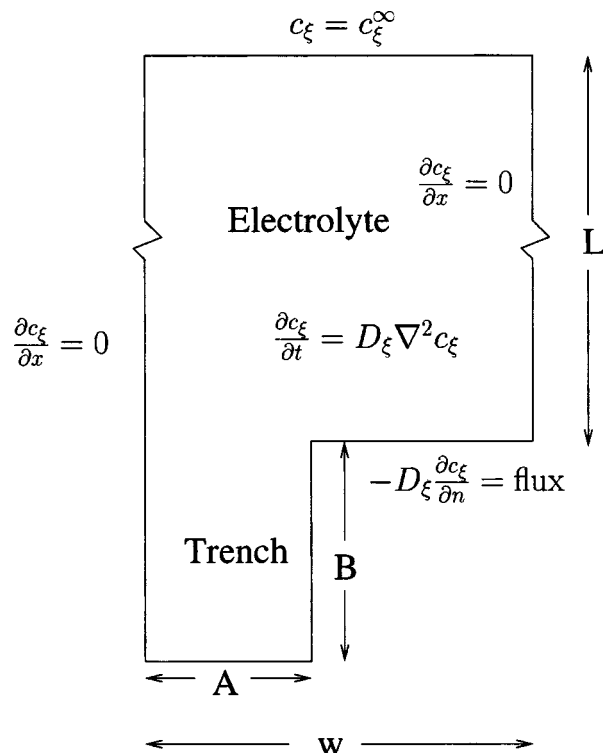


Figure 1. Solution domain and boundary conditions.

proportion of available sites. Note, for comparison to Ref. 7, the rate constant used here, k_a , has been multiplied by Γ_0 , the saturation site density. The consumption flux is given by

$$J_d = \frac{k_d}{\Gamma_0} \theta^n \quad [7]$$

where k_d is the consumption rate constant. J_d represents an n th order consumption process, here $n \approx 3$. The rate constants, k_a and k_d , are functions of the overpotential η . The parameter values for Eq. 3, 4, 6, and 7 are obtained entirely from (i - η) voltammetry on flat copper electrodes,⁷ independent of trench-filling experiments. The concentration of the cupric ion and accelerator in the electrolyte are governed by diffusion such that

$$\frac{\partial c_\xi}{\partial t} = D_\xi \nabla^2 c_\xi \quad [8]$$

where t is time, $c_\xi = c_\xi^\infty$ outside of the boundary layer of depth δ and D is the diffusion coefficient. The subscript ξ is given by

$$\xi = \begin{cases} m & \text{for accelerator} \\ c & \text{for } \text{Cu}^{2+} \end{cases} \quad [9]$$

The flux loss from the electrolyte at the interface is given by

$$-D_\xi \frac{\partial c_\xi}{\partial n} = \begin{cases} -k_a(1 - \theta) c_m^i & \text{for accelerator} \\ -v(V_c - c_c^i) & \text{for } \text{Cu}^{2+} \end{cases} \quad [10]$$

where V_c is the moles per volume of solid copper. The solution domain and boundary conditions are illustrated in Fig. 1. The aspect ratio of the trench and the trench spacing are given by $B/2A$ and $2w$, respectively. The main approximation of the model geometry compared with the experimental configuration is the assumption of an infinite set of trenches. Typically experimental configurations con-

sisted of ≈ 100 trenches with $w \approx 1 \mu\text{m}$. The model symmetry condition is a good approximation under these conditions.

Level set equation.—In the model proposed here, $\phi = 0$ marks the position of the interface. The variable ϕ is continuous and monotonic in the region near the interface. The advection equation describing the motion of the interface can be written

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = 0 \quad [11]$$

with the interface normal given by

$$\mathbf{n} = \frac{\nabla \phi}{|\nabla \phi|} \quad [12]$$

Since $\mathbf{v} = v\mathbf{n}$ with $v = |\mathbf{v}|$, Eq. 11, can be rewritten

$$\frac{\partial \phi}{\partial t} + v|\nabla \phi| = 0 \quad [13]$$

During the evolution of the interface ϕ is maintained as a distance function. Initially this is accomplished by solving

$$|\nabla \phi| = 1 \quad [14]$$

The use of extension velocities inhibits the requirement for reinitialization, improving efficiency and accuracy.¹² The extension velocities are constructed by solving

$$\nabla v_{\text{ext}} \cdot \nabla \phi_{\text{temp}} = 0 \quad [15]$$

with $v_{\text{ext}} = v$ at $\phi = 0$ and ϕ_{temp} is calculated between every time step using Eq. 14. Thus, without loss of accuracy at $\phi = 0$, Eq. 13 can be rewritten

$$\frac{\partial \phi}{\partial t} + v_{\text{ext}}|\nabla \phi| = 0 \quad [16]$$

The solution of Eq. 14 and Eq. 15 to find v_{ext} between timesteps enables Eq. 16 to maintain ϕ as a distance function without directly recalculating ϕ between timesteps, thus avoiding reinitialization issues. The fast marching method is used to solve Eq. 14 and 15. This is a well-documented method and further details can be found in Ref. 12.

Conservation of accelerator.—In order to model the accelerator as a surfactant it is necessary to recast the conservation Eq. 5 from a Lagrangian to an Eulerian framework in the following manner

$$\frac{d}{dt} \int_u \theta dA_u = \frac{d}{dt} \int_u \theta |\nabla \phi| \delta(\phi) dV_u \quad [17]$$

$$= \int_{\text{fix}} \left(\frac{\partial \theta}{\partial t} + v_{\text{ext}} \nabla \cdot (\mathbf{n}\theta) \right) |\nabla \phi| \delta(\phi) dV_{\text{fix}} \quad [18]$$

using $\nabla \phi \cdot \nabla v_{\text{ext}} = 0$ and $\dot{\phi} = 0$. The subscripts u and fix refer to Lagrangian and Eulerian frameworks, respectively. Equation 17 recasts the integral from a surface-to-volume integral while Eq. 18 moves from a control volume moving with the interface to a control volume fixed in space. In weak form, around $\phi = 0$, the conservation equation is written

$$\frac{\partial \theta}{\partial t} + v_{\text{ext}} \nabla \cdot (\mathbf{n}\theta) = J_a - J_d \quad [19]$$

Discretization

The finite difference equations are derived for a nonuniform cell-centered unstructured mesh using the finite volume method as first introduced by Patankar.¹³ Integrating over a control volume (CV),¹⁴

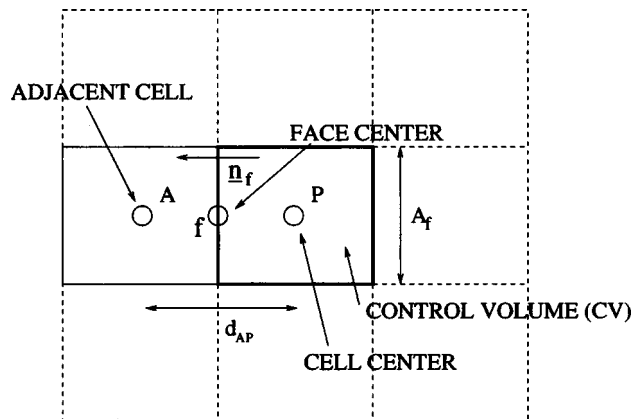


Figure 2. A CV structure showing the control volume (CV), at whose center the variables are being evaluated, and the adjacent cell.

applying the divergence theorem to the diffusion term and adding a source term, Eq. 8 can be rewritten (dropping the ξ)

$$\int_V \frac{\partial c}{\partial t} dV = \int_{\partial V} D \mathbf{n} \cdot \nabla c d(\partial V) + \int_V S dV \quad [20]$$

where S is the source term, V is the CV volume, and $\mathbf{n}$ is the normal to the bounding surface ∂V . An illustration of a CV structure can be seen in Fig. 2. The source term is typically linearized such that

$$S = S_C + c_P S_P \quad [21]$$

where c_P , S_C , and S_P are the variable value at the cell center, the constant source coefficient, and the variable source coefficient, respectively. The subscript P refers to the volume-averaged cell value. Using a first-order implicit scheme, Eq. 20 can be discretized such that

$$\frac{(c_P - c_P^0)V_P}{\Delta t} = \sum_f D_f A_f \frac{c_A - c_P}{d_{PA}} + S_C V_P + S_P c_P V_P \quad [22]$$

where c_P^0 , V_P , Δt , D_f , A_f , c_A , d_{PA} are the previous time-step value of c_P , cell volume, time step size, diffusion coefficient at the face, face area, adjacent variable value, and distance between cell centers, respectively. The subscript A refers to the adjacent averaged cell value. The summation $\sum_f$ is over all cell faces, f , of the CV. Eq. 22 can now be rewritten in the form

$$a_P c_P = \sum_f a_A c_A + b_P \quad [23]$$

where

$$a_P = V_P - S_P V_P \Delta t + \sum_f \frac{D_f A_f \Delta t}{d_{PA}} \quad [24]$$

$$a_A = \sum_f \frac{D_f A_f \Delta t}{d_{PA}} \quad [25]$$

and

$$b_P = \Delta t S_C V_P + c_P^0 V_P \quad [26]$$

The diffusion coefficient at a face is given by the harmonic mean such that

$$D_f = \frac{d_{AP} D_P D_A}{d_{AP} D_P + d_{AP} D_A} \quad [27]$$

where d_{Af} and d_{fp} are the distances between the adjacent cell centers and the dividing face. Equation 23 can be written in matrix form

$$\mathbf{Ax} = \mathbf{b} \quad [28]$$

where $\mathbf{A}$, $\mathbf{x}$, and $\mathbf{b}$ are the coefficient matrix, solution column vector, and source column vector, respectively. In this form, Eq. 28 can be solved using any sparse iterative technique. In this paper, a conjugate gradient solver is used with Jacobi preconditioning. Since advection is normal to the interface, between time steps, the discretized version of Eq. 16 given by

$$\phi_P = \phi_P^O + |\nabla\phi|v_{\text{ext},P}\Delta t \quad [29]$$

can be used to update ϕ . The term $|\nabla\phi|$ can be evaluated with a first or second order scheme using upwinding with the characteristics $v_P\nabla\phi$.¹² Both first and second order schemes were evaluated, and no significant improvement with second order was observed with regard to the simulations in this paper. The movement of the interface must satisfy a stability criterion. Essentially the interface should not move more than one grid space per time step to maintain stability. The Courant-Friedrichs-Lewy (CFL) stability number is given by

$$\sigma_{\text{cfl}} = \max\left(\frac{v_P\Delta t}{d_{AP}}\right) \quad [30]$$

The stability criterion states that $\sigma_{\text{cfl}} < 1/\sqrt{N}$ for the numerical scheme to converge, where N is the spatial dimension of the geometry ($N = 2$ in this case).

In order to evaluate boundary conditions on the copper/electrolyte interface it is necessary to define an interface depth and a Dirac-delta function. The depth of the interface is defined to be 2ϵ , such that

$$\epsilon = \frac{\Pi_i d_{AP}}{\sum_{f_i}(1 - \mathbf{n} \cdot \mathbf{n}_{f_i})\Pi_{(f_j - f_i)}d_{AP}} \quad [31]$$

where $\Pi_{(f_j - f_i)}$ represents the product over all faces other than f_i . The delta function is evaluated from ϕ such that

$$\delta(\phi) = \begin{cases} 0 & \text{if } |\phi| > \epsilon \\ [1 + \cos(\pi\phi/\epsilon)]/2\epsilon & \text{if } |\phi| \leq \epsilon \end{cases} \quad [32]$$

The interface boundary conditions given in Eq. 10 can now be defined as linearized source terms. The constant source coefficient, S_C , is written

$$S_C = \begin{cases} 0 & \text{for accelerator} \\ 0 & \text{for } \text{Cu}^{2+} \end{cases} \quad [33]$$

and the variable source coefficient, S_P , is written

$$S_P = \begin{cases} -k(1 - \theta)\delta(\phi)|\nabla\phi| & \text{for accelerator} \\ -(V_c - C_c^i)v_{\text{ext}}\delta(\phi)|\nabla\phi|/c_c^* & \text{for } \text{Cu}^{2+} \end{cases} \quad [34]$$

where the superscript* refers to the previous sweep value within the iterative solver. The form of the source term chosen in Eq. 34 maintains stability by increasing the diagonal coefficient a_P . The diffusion coefficients are defined to be

$$D = \begin{cases} 0 & \text{if } \phi < -\epsilon \\ D_\xi & \text{if } \phi \geq -\epsilon \end{cases} \quad [35]$$

to account for diffusion only in the electrolyte-filled region ($\phi \geq -\epsilon$). Without loss of generality at the interface, Eq. 19 can be split and solved separately in various regions of the domain. Equation 19 is written

$$\frac{\partial\theta}{\partial t} = 0 \quad \text{for } \phi < 0 \quad \text{or } \phi > 2\epsilon \quad [36]$$

$$\frac{\partial\theta}{\partial t} + v_{\text{ext}}\nabla \cdot (\mathbf{n}\theta) = \frac{k_a c_a}{\Gamma_0}(1 - \theta) - \frac{k_d}{\Gamma_0}\theta^3 \quad \text{for } \phi = 0 \quad [37]$$

$$\nabla \cdot (\mathbf{n}\theta) = 0 \quad \text{for } 2\epsilon \geq \phi > 0 \quad [38]$$

Equations 36, 37, and 38 are discretized in the general way as outlined in Eq. 22. The second term in Eq. 37 is discretized in a standard finite volume (FV) upwind manner for a convection term with characteristics $(\mathbf{n}_f \cdot \mathbf{n})$, effectively upwinding θ forward from the interface. The source terms are linearized in such a way that the gradient with respect to the solution variable is preserved. The discretization for Eq. 37 is as follows

$$a_P = \frac{V_P}{\Delta t} + \sum_f \frac{\max(\phi_A - \phi_P, 0)v_{\text{ext},P}A_f}{d_{AP}|\nabla\phi|_f} + \frac{k_a c_{CP}V_P}{\Gamma_0} + 3\theta_P^{*2}k_dV_P \quad [39]$$

$$a_A = -\sum_f \frac{\min(\phi_A - \phi_P, 0)v_{\text{ext},P}A_f}{d_{AP}|\nabla\phi|_f} \quad [40]$$

$$b_P = \frac{V_P}{\Delta t} + \frac{k_a c_{AP}V_P}{\Gamma_0} + 2\theta_P^{*3}k_dV_P \quad [41]$$

Equations 39 and 40 contain min and max conditional statements to preserve the upwinding requirement for the convection term in Eq. 37. Equation 37 is solved in the normal way during the sweep cycle with the other variables, however this is only undertaken for cells adjacent to the interface. Equation 38 is discretized in a similar manner to Eq. 37. This equation is not updated during the sweep but solved with the extension velocities with the use of the fast marching method. Details of the fast marching method can be found in Ref. 12.

Validation

This section contains three validation test cases that test various parts of the numerical algorithm. The test cases are as follows: Case 1: accelerator adsorption validation to test the rate of accumulation of θ from the electrolyte. Case 2: accelerator coverage change due to arc length change on an expanding and contracting circle without accumulation and with constant velocity. Case 3: comparison between the LSM and a string model for superconformal electrodeposition.

Case 1: accelerator adsorption validation.—In the case of an advancing planar interface a one-dimensional analytical solution can be found for the accumulation of accelerator at the copper/electrolyte interface as well as the concentration of accelerator throughout the electrolyte. This analytical solution is compared with a numerical test case. The diffusion equation, Eq. 8, for accelerator in one-dimension is written

$$c_t = Dc_{xx} \quad [42]$$

with boundary conditions of $c = c^\infty$ at $x = L$ and

$$Dc_x = kc(1 - \theta) \quad [43]$$

at $x = 0$. The accumulation of accelerator at the interface for a planar front has no dependence on curvature, thus Eq. 5 becomes

$$\dot{\theta} = \frac{kc}{\Gamma_0}(1 - \theta) \quad [44]$$

with an initial condition of $\theta = 0$ at $t = 0$. From Eq. 42 and Eq. 44 diffusion and interface kinetic time scales can be found such that

Table I. The parameters used for the advancing front test case approximating interface-limited accumulation when $M \gg 1$.

Parameter	Value	Unit
c^∞	1×10^{-4}	mol/m ³
D	1×10^{-9}	m ² /s
Γ_0	1×10^{-5}	mol/m ²
L	1×10^{-4}	m
k	8.4×10^3	m/s
M	1.2×10^3	dimensionless

$$t_{\text{diff}} = \frac{L^2}{D} \quad [45]$$

and

$$t_{\text{kin}} = \frac{\Gamma_0}{kc^\infty} \quad [46]$$

respectively. By comparing Eq. 45 and Eq. 46 a dimensionless number, M , can be written for the relative importance of the diffusion vs. the interface kinetics, and is given by

$$M = \frac{t_{\text{kin}}}{t_{\text{diff}}} = \frac{D\Gamma_0}{L^2kc^\infty} \quad [47]$$

When $M \gg 1$ the problem is said to be interface limited. In this limit the transient term in Eq. 42 can be dropped leading to a simple closed form expression for $c[x, \theta(t)]$ and an implicit expression for $\theta(t)$ given by

$$c = \frac{c^\infty[1 + k(1 - \theta)x/D]}{1 + kL(1 - \theta)/D} \quad [48]$$

and

$$-D \ln(1 - \theta) + kL\theta = \frac{kDc^\infty t}{\Gamma_0} \quad [49]$$

When $M \ll 1$ accumulation is said to be diffusion limited, and the diffusive term in Eq. 42 can be dropped. The solutions in this limit are given by

$$c = c^\infty \frac{\exp[k(1 - \theta)x/D]}{\exp[k(1 - \theta)L/D]} \quad [50]$$

and

$$E_i(Lk/D) - E_i[Lk(1 - \theta)/D] = \frac{kc^\infty t}{\Gamma_0} \quad [51]$$

Using physically relevant parameters, see Table I, the numerical solution was compared with the expressions from Eq. 48 and Eq. 49 for interface-limited kinetics. The comparison for the accelerator coverage, θ , over time can be seen in Fig. 3. Three mesh densities of 10, 50, and 100 elements were used across the boundary layer with thickness L , each five elements wide along the planar front. The numerical results are independent of mesh density for 50 and 100 elements indicating convergence. The curves for the converged numerical and analytical results compare well for $\theta(t)$. The slight difference is due to the analytical approximation implicit in the finite value of M , see Table I. The one-dimensional accelerator concentration in the electrolyte can be seen in Fig. 4. The comparison between the analytical expression and the 100 element mesh at times of 933 and 19,933 s again shows good agreement. The mesh spacing is fine in the region of the interface and is gradually increased as $x \rightarrow L$. The front is advancing with a velocity of 1.25×10^{-11} m/s. Over

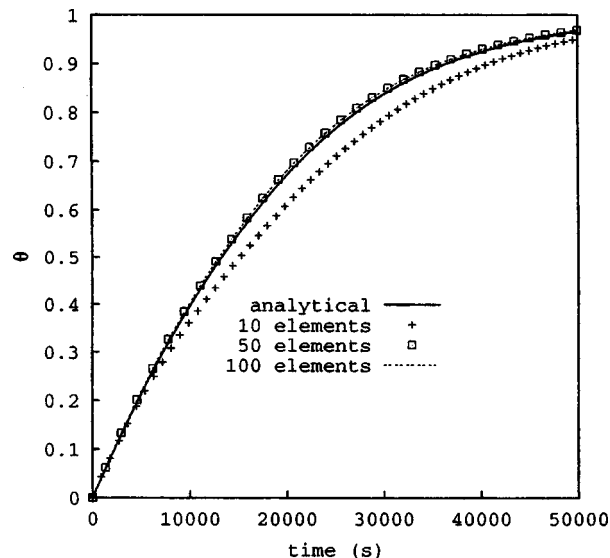


Figure 3. Comparison between the numerical and analytical solution for one-dimensional accelerator adsorption for a case where accumulation is limited by interface kinetics.

the complete simulation of 50,000 s the advancing front has covered 50 elements of the 100 element mesh with $\sigma_{\text{eff}} = 0.1$.

Case 2: accelerator coverage change on an expanding and contracting circle.—An expanding and contracting circle is used as a test case for the accuracy and convergence properties of the curvature-based accumulation model for the accelerator. Given a circle with initial coverage θ_0 and radius r_0 at $t = 0$, conservation of the accelerator dictates that the coverage at any subsequent time can be written

$$\theta = \frac{\theta_0 r_0}{r_0 + vt} \quad [52]$$

where v is the constant velocity magnitude of the circle interface. The test case domain consists of a 1 by 1 region enclosing circles

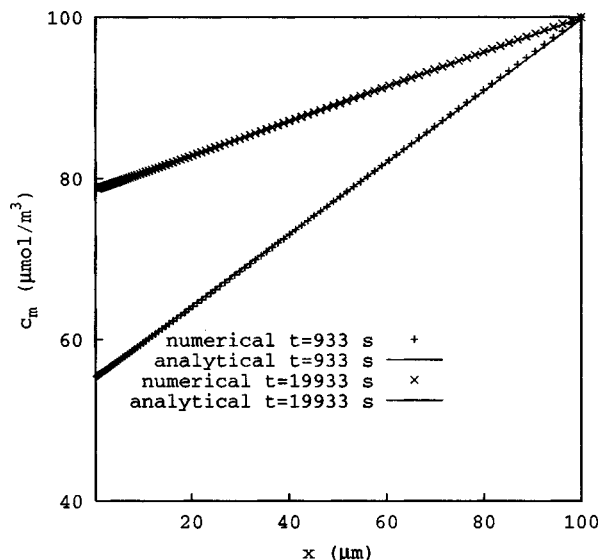


Figure 4. Comparison between the numerical and analytical solutions for accelerator concentration in the electrolyte at times of 933 and 19,933 s for a case where accumulation is limited by interface kinetics.

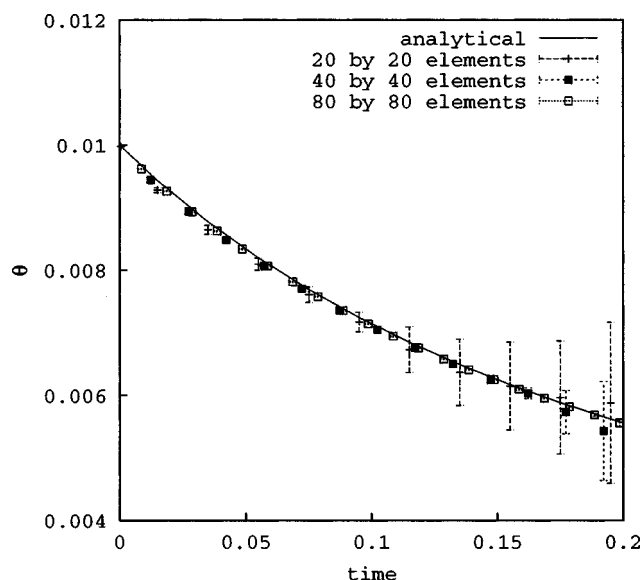


Figure 5. Comparison between the numerical and analytical solution for the expanding circle test case for various mesh densities. The analytical curves are shown as solid lines while the numerical solutions are denoted by symbols that depend on the given mesh density. The error bars denote the maximum and minimum values of θ on the circle.

with initial conditions, $\theta_0 = 0.01$, $v = 1$, $r_0 = 0.25$ for the expanding circle, $r_0 = 0.35$ for the contracting circle, and $\sigma_{\text{cfl}} = 0.1$. Meshes of 20 by 20, 40 by 40, and 80 by 80 elements were used in each case. The test case results can be seen in Fig. 5 and 6 for the expanding and contracting circles, respectively. In the expanding test case the results show good agreement for each mesh density. The maximum and minimum values of θ begin to diverge at $t = 0.1$ for the 20 by 20 element mesh and at $t = 0.16$ for the 40 by 40 element mesh. The 80 by 80 element mesh remains close to the analytical solution until the interface reaches the edge of the do-

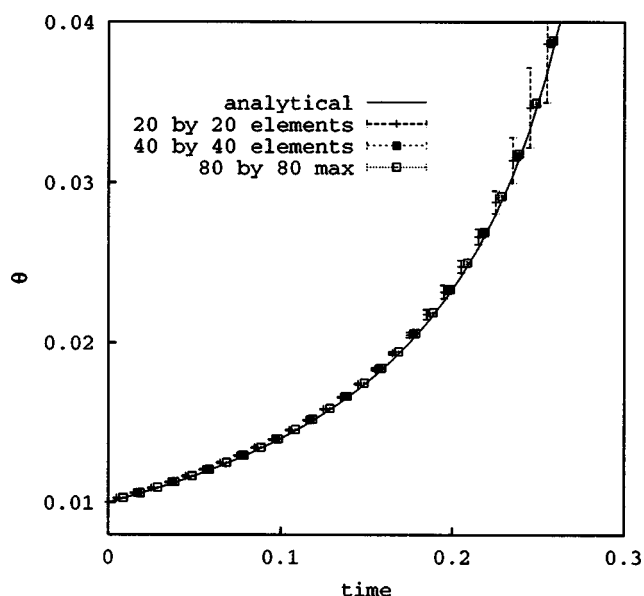


Figure 6. Comparison between the numerical and analytical solution for the contracting circle test case for various mesh densities. The analytical curves are shown as solid lines while the numerical solutions are denoted by symbols that depend on the mesh density. The error bars denote the maximum and minimum values of θ on the circle.

Table II. Material parameters for the comparison of the level set and string models.

Parameter	Value	Unit
C_{mpsa}^{∞}	5×10^{-3}	mol/m ³
Γ_0	1×10^{-5}	mol/m ²
L	1.5×10^{-4}	m
η	-0.2	V
σ_{cfl}	0.1	Dimensionless
Aspect ratio	3	Dimensionless
Trench depth	5×10^{-7}	m

main. In the contracting test case the 20 by 20 element mesh begins to diverge at $t = 0.22$. Results from both the 40 by 40 and 80 by 80 element meshes remain close to the analytical solution until the interface collapses in on itself at which time the coverage becomes infinite. These test cases demonstrate the accuracy of the LSM numerical solution in simulating the CEAC-based model.

Comparison between the level-set method and a string model.—In previous work a string model (particle marker method) based on the CEAC mechanism for superconformal deposition was developed.² The string model determined the interface position and accelerator coverage assuming a nonzero starting value and local conservation of the accelerator. It used bulk concentration of cupric ion in the electrolyte, ignoring depletion due to diffusion gradients. Here results from the string model, modified to include additive accumulation and using interface kinetics identical to those for the LSM model, are compared with the LSM results for superconformal filling. In order to permit meaningful comparisons concentration gradients were eliminated from the LSM by using infinite diffusion coefficients for both accelerator and cupric ion. The other physical parameters for this study are presented in Table II. Figure 7 shows a comparison between the LSM and string models for the height of the bottom surface of the trench with time. Both models were checked for mesh independence at their respective mesh densities of 8,000 points in the string model and 192,000 elements in the LSM model. Figure 7 shows the agreement is excellent between the two models with the exception of the formation of the overfill bump.

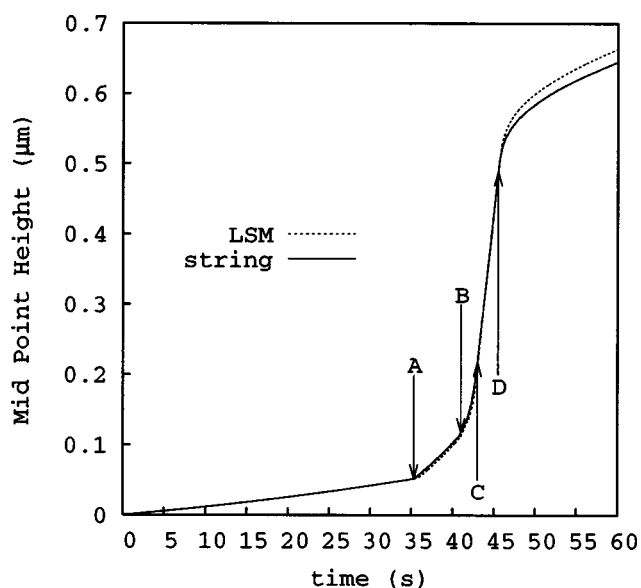


Figure 7. Comparison between the LSM and string model for the height of the midpoint of the trench with an aspect ratio of three and a depth of 0.5 μm . Both models show excellent agreement for the rapid filling of the trench from the bottom up. Transition points between the various fill regimes are marked.

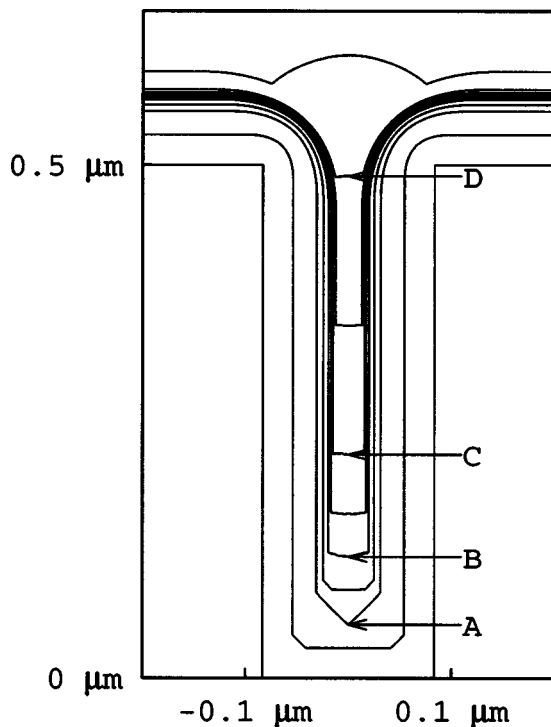


Figure 8. The interface evolution at various stages of fill. The letters mark the transition points between the fill regimes.

Both models capture the important transition in filling behavior marked by the letters in Fig. 7 and 8. Figure 8 shows various stages of interface evolution as the trench is filling. Initially before transition A there is a period of conformal growth during which the corners of the trench form diagonal sections. These diagonal sections meet at transition A and form a flat base which rises steadily until transition B. Here the bottom surface velocity increases until transition C where the surface has maximum coverage. Transition D occurs when the sidewall spacing begins to increase, thus increasing the overall surface area and slowing the bottom height velocity. The difference between the two models above the height of 0.5 μm in Fig. 7 is due to the difficulty of accurately modeling the surfactant coverage on the spreading interface (note the large change in area, Fig. 8).

Modeling and Experimental Comparison for Copper Electrodeposition

Interface evolution for a variety of deposition and geometric parameters was simulated for comparison with experimental results. The goal was to predict a parameter space, (η, c_m^∞) , for which superfill occurs at high aspect ratios. The type of filling, ranging from conformal to superfill, can be determined from the presence/absence of voids in the filled trench as well as features, such as cusps and bumps, that form above the trench during deposition. Experimentally, there is some variation in the formation of these features under nominally identical conditions due to uncontrolled experimental differences. However it is generally clear when superfill occurs for particular parameters. For example, the superfill behavior in Fig. 9c manifests as both trench filling and an overfill bump that are experimentally reproducible. Both filling and deposition features can be used for semiquantitative determination of model accuracy.

In the experiments, Fig. 9, the aspect ratios of the patterned trenches are approximately 1.5, 1.9, 2.5, 3.3, and 4.6 with a trench depth of 0.46 μm . To permit electrodeposition, a copper seed layer is first applied by a vacuum deposition technique. This application is difficult on the sides of high aspect ratio features. For example, a 6 nm thick Cu seed on each sidewall requires deposition of 0.1 μm of

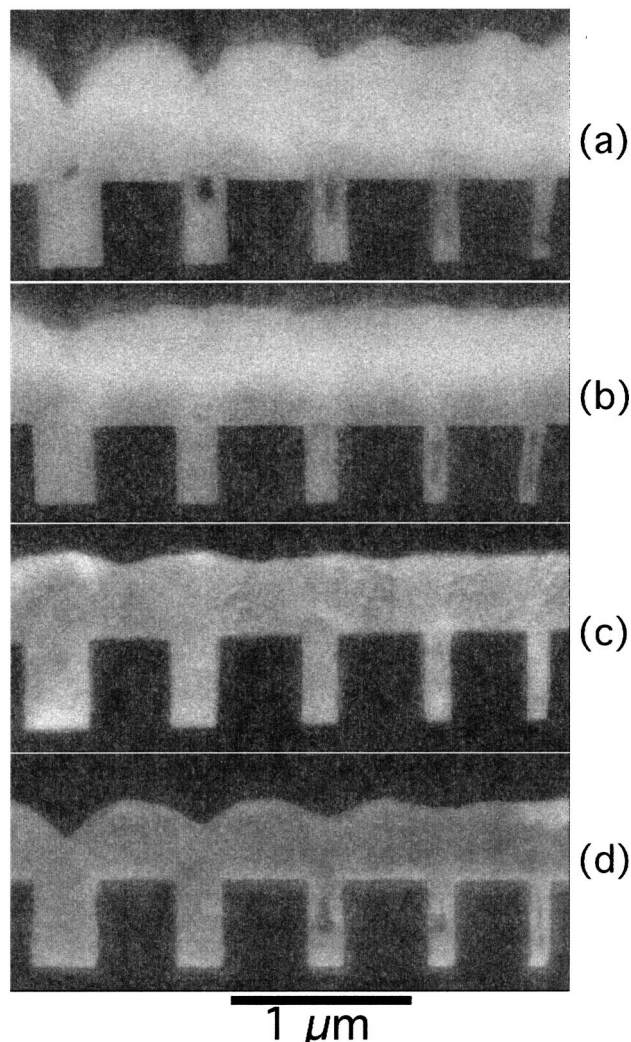


Figure 9. SEM images of trenches filled from electrolytes with c_m^∞ : 0, 0.0005, 0.005, and 0.04 mol/m^3 and overpotentials η : -0.097 , -0.301 , -0.282 , and -0.150 V [top (a) to bottom (d)], and aspect ratios (with Cu seed): 1.8, 2.3, 3.0, 4.0, 5.6 (left to right).

Cu over the trench. The effective trench depth for electrodeposition is thus 0.56 μm and the aspect ratios increase to approximately 1.8, 2.3, 3.0, 4.0, and 5.6. The substrates used for the depositions measured 1 cm^2 with a patterned area of 50 by 50 μm and trench spacing of ≈ 0.5 μm . The first set of trenches, Fig. 9a, show the poor filling that occurs when no additive is present in the electrolyte, $c_m^\infty = 0$ mol/m^3 . Voids are evident in all trenches. The filling is conformal until the unfilled region of the trench becomes sufficiently

Table III. Material and geometric parameters used for the simulations for comparison with experiment.

Parameter	Value	Unit
B	0.46	μm
w	5.0	μm
c_c^∞	250.0	mol/m^3
V_c	0.141×10^6	mol/m^3
Γ_0	9.8×10^6	mol/m^2
σ_{cfl}	0.1	
δ	1.5×10^{-5}	m
D_{Cu}	5.0×10^{-10}	m^2/s
D_{mpsa}	1.0×10^{-9}	m^2/s

Table IV. Experimental parameters obtained by best fit analysis of cyclic voltammetry to determine θ dependence. The table values are for kinetic parameters in an electrolyte with additives. The site density Γ_0 is the saturation packing of the accelerator (roughly one-third of metal sites) on a copper (111) surface.

Parameter	Value	Unit
b_0	0.69	A/m ²
b_1	6.4	A/m ²
m_0	0.447	Dimensionless
m_1	0.299	Dimensionless
k_a	$1.76\text{--}245 \times 10^{-6}\eta^3$	m/s
k_d	0.0	m/sV ³
Γ_0	9.8×10^{-6}	mol/m ²

narrow that the deposition rate decreases going down the trench. The differential deposition rate causes the sidewalls to bulge and neck near the top of the trench creating a void. Voiding in the second set of trenches, Fig. 9b, is significantly reduced by the inclusion of additives in the electrolyte. Selection of near-optimal additive concentrations leads to optimal filling, Fig. 9c. Excessive additive concentration results in a reversion to conformal deposition, Fig. 9d. Trenches which contain voids characteristically have a cusp over them while those that fill have a bump. Trenches without a void but with a cusp above them, (Fig. 9d, aspect ratio 2.5), typically contain a seam or a very thin void.

Parameters that correspond to the experimental conditions are presented in Tables III and IV. The additive-free parameters are given separately in Table V. Simulations were performed using the values contained in these tables. The trench spacing was modeled with a value of $w = 1 \mu\text{m}$, giving only a slight overlap of diffusion fields, due to the small fraction of the specimen surface area that was perturbed due to trench patterning. The simulations, Fig. 10 show good agreement with experiment, accurately predicting the formation of voids, cusps, and bumps. In the ($\eta = -0.097 \text{ V}$, $c_m^\infty = 0.0 \text{ mol/m}^3$) case, Fig. 10a, deposition is entirely conformal as expected with no additive. All simulations result in voids in agreement with experiments. For the ($\eta = -0.301 \text{ V}$, $c_m^\infty = 0.0005 \text{ mol/m}^3$) case, Fig. 10b, deposition is predicted to be essentially conformal. In this case, the dilute concentration causes close-off to occur before the CEAC mechanism becomes significant. This leads to voids in all the trenches. In the ($\eta = -0.15 \text{ V}$, $c_m^\infty = 0.04 \text{ mol/m}^3$) case, Fig. 10d, significant acceleration by the CEAC mechanism occurs at the bottom of the trench as required for superfill. However, accelerator coverage on the sidewalls builds up almost as quickly through simple accumulation due to the high accelerator concentration in the electrolyte. This effect is aggravated by the slow base velocity at low overpotentials. This leads to marginal failure in the trench of aspect ratio 3 and voids in aspect ratios of 4 and 5.6. In the ($\eta = -0.282 \text{ V}$, $c_m^\infty = 0.005 \text{ mol/m}^3$) case, Fig. 10c, superfill is predicted to occur for all but the finest features.

Table V. Experimental parameters obtained by best fit analysis of cyclic voltammetry to determine θ dependence. The table values are for kinetic parameters in an electrolyte with no additives. The site density Γ_0 is the saturation packing of the accelerator (roughly one-third of metal sites) on a copper (111) surface.

Parameter	Value	Unit
b_0	3.0	A/m ²
b_1	0.0	A/m ²
m_0	0.5	Dimensionless
m_1	0.0	Dimensionless
k_a	$1.76\text{--}245 \times 10^{-6}\eta^3$	m/s
k_d	0.0	m/sV ³
Γ_0	9.8×10^{-6}	mol/m ²

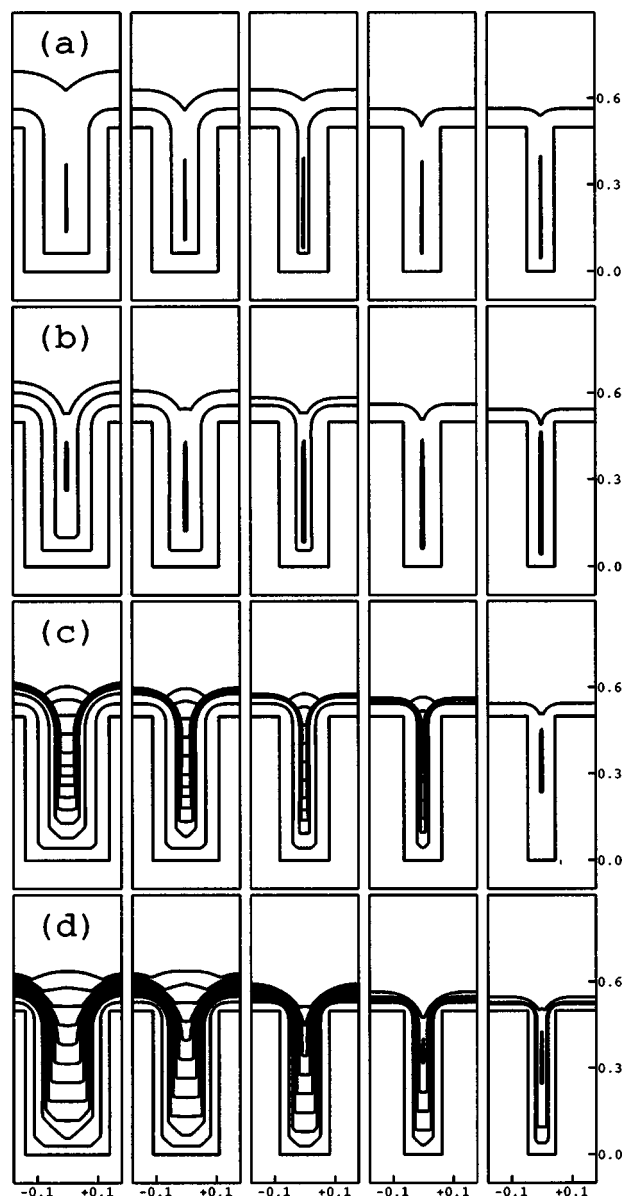


Figure 10. Simulations of copper deposition in trenches with c_m^∞ : 0, 0.0005, 0.005, and 0.04 mol/m³ and overpotentials η : -0.097 , -0.301 , -0.282 , and -0.150 V [top (a) to bottom (d)], and aspect ratios: 1.8, 2.3, 3.0, 4.0, 5.6 (left to right). Voids occur for all the (a) and (b) sets of trenches, the finest (c) trench and the two finest (d) trenches. The only other trench not to fill is the (d) trench with aspect ratio of three. All units are in micrometers. Parameters for these simulations are given in Tables III, IV, and V.

Here the accumulation and overpotential-dependent base velocity combined appropriately to give rapid enhancement of accelerator coverage only on the bottom of the filling feature. Though the experimental image, Fig. 9c, appears to indicate fill in all features for these conditions, it is likely that the finest feature does in fact contain a fine seam.¹

Each simulation was performed with a mesh of 116,337 elements and took 3 days on a 1.2 GHz processor.

Conclusions

The level set implementation of the CEAC mechanism represents a novel numerical approach. The method effectively predicts superconformal deposition in the copper Damascene process, specifically helping to understand the dynamic periods of conformal growth, accelerated bottom-up growth, and the overfill bump formation. Ad-

ditional phenomena such as consumption and surface diffusion could be readily included in the model once required physical parameters are obtained from experiments. Recently this model was used to predict superconformal electrodeposition for silver.¹⁵ Further work will extend the model for filling of three dimensional vias.

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List of Symbols

A_f	face area
A_u	interface area
b_0	experimentally determined parameter
b_1	experimentally determined parameter
c_A	adjacent variable value
c_c^∞	far field copper concentration
c_c^i	interface copper concentration
c_m^i	interface accelerator concentration
c_p	cell center value
c_p^0	previous time-step value of c_p
d_{Af}	distance between cell center and face
D	diffusion coefficient
D_f	diffusion coefficient at the face
d_{pA}	distance between cell centers
F	Faraday's constant
i	current density
i_0	exchange current density
J_a	adsorption flux
J_d	consumption flux
k_a	adsorption rate constant
k_d	consumption rate constant
m_0	experimentally determined parameter
m_1	experimentally determined parameter
M	dimensionless parameter
$\mathbf{n}$	interface normal
R	gas constant
S_C	constant source coefficient
S_p	variable source coefficient
S	source term
t_{diff}	diffusion timescale
t_{diff}^k	kinetic timescale
T	temperature
t	time

V_c	moles per volume of copper
v	interface velocity
v_{ext}	extension velocity
V_p	cell volume
V	control volume

Greek

α	transfer coefficient
Γ_0	surface site density
Δt	time step size
δ	delta function
∂V	control volume surface
ϵ	local interface depth
η	overpotential
θ	accelerator coverage
σ_{cfl}	CFL number
ϕ	level set variable
Ω	atomic volume

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